STAT

Approved For Release 2009/08/17 : CIA-RDP88-00904R000100100

Third United Nations
International Conference
on the Peaceful Uses
of Atomic Energy

A/CONF.[illegible]/P/[illegible]
USSR
May 1964
Original: RUSSIAN

Confidential until official release during Conference

"CHEMICAL AND ELECTROCHEMICAL BEHAVIOUR OF
TECHNETIUM IN AQUEOUS SOLUTIONS"

by

Vict.I.Spitsyn, A.Th. Kuzina, N.N.Zamoshnikova, A.A.Oblova

Introduction

The report is devoted to the study of the chemical and electrochemical characteristics of technetium, separated in laboratory conditions from neutron-irradiated metallic molybdonum and from industrial nitrate waste solution.

The most important problems in the chemistry of technetium are syntheses of its compounds for diverse states of valency, as well as the study of conditions of their stabilization in solutions. The identification and examination of technetium compounds are embarrassed up to now by the lack of data on the absorption spectra characteristic for many valence forms of Tc. The capacity to manifest several oxidation degrees, the easiness of their reciprocal transitions, sometimes the simultaneous presence in solution of ions of different valence complicate the work with technetium. It needs besides to take in account some other particularities of Tc, such as disproportionation and complexformation (1-17).

1. The concentration of technetium from molybdate and industrial waste nitrate solutions

For getting out technetium both from neutron-irradiated molybdenum and from waste solutions of uranium reprocessing we have used the extraction methods.

The use of acetone for concentration of technetium from the waste nitrate solutions, containing great amounts of fission fragments, some quantity of macroadmixtures and products of equipment corrosion, affords the possibility to separate almost radiochemically pure technetium already from the first extraction stage (table I) and to reach the high decontamination factor of the order 10^4 (table II), as well as considerable deliverance from the macroadmixtures.

All the more in the case of molybdate solutions(2) with little content of radiochemical impurities it was not difficult to separate the radiochemically pure technetium by means of acetone. The use of quinoline and tributylphosphate as extractives also results in good success.

The calculation of the quantity of theoretical stages by the use of acetone, quinoline and tributylphosphate has shown, that in capacity of laboratory equipment simply designed uncomplicated extractors of the mixer-settler type would fit for this purpose. The average stage quantity corresponds to 2 - 4.

The extraction of technetium from aqueous solutions was carried out under following conditions: for acetone - at 3N alkalinity calculating on NaOH, for quinoline - at pH=11,8, for TBP - at 0,5 N alkalinity calculating on HNO_3. Isolation of technetium was realized from acetone by distilling off the extractive; for quinoline - by reextracting with chloroform into water; from tributylphosphate - by reextracting with 10 N nitric acid or 5 N solution of NaOH.

349

Approved For Release 2009/08/17 : CIA-RDP88-00904R000100100048-8

Table I

The radiochemical composition of acetone extracts from industrial nitrate solutions

The volume of initial solution = 1 L,
The acetone volume = 0,5 L.

Samples	Extract Nr	Activity mCu/ml. 10^4	Isotope contents, % Tc^{99}	Ru^{106}	Cs^{137}
1	1	8,5	91	7	2
	2	2,1	83	7	10
	3	0,6	43	18	39
II	1	9,0	87	6	7
	2	8,5	52	35	13
	3	3,0	27	18	55
III	1 + 2	3,6	97	-	3
	3	5,2	16	58	26

Table II

The technetium extraction from industrial nitrate solution with acetone, quinoline, tributylphosphate and isoamyl alcohol[x)]

Volume of initial solution=1 L, extractive reagent volume = 0,5 L.

Extractive reagent	Decontamination factor	Technetium content in organic phase %
Acetone	10^4	98
Quinoline	10^3	58
[illegible]	10^2	56
Isoamyl alcohol	10	60

x) There was made a thrice-repeated extraction followed by washing the extractive reagent. Technetium content of initial solution was assumed to be = 100%.

349

Approved For Release 2009/08/17 : CIA-RDP88-00904R000100100048-8

2. The preparation of pure compounds of technetium and methods of their analysis

The concentrates of technetium obtained by extraction method were treated by hydrochloric acid. The end acidity of medium corresponded to 1 - 2 N calculating on HCl. From such a solution there was precipitated with H_2S the dark brown technetium heptasulphide, Tc_2S_7, which was then transformed by treatment with mixture of hydrogen peroxide and ammonia into soluble ammonium pertechnate NH_4TcO_4 and thereupon into sparingly soluble compound tetraphenylarsonium pertechnate $(C_6H_5)_4AsTcO_4$. The latter was reduced with hydrogen at the temperature 260–280° into dioxide TcO_2.

From technetium dioxide by oxidation with hydrogen peroxide in ammonia medium and following eliminating the excessive ammonia by evaporation ammonium pertechnate was obtained in crystalline form.

Technetium metal was prepared by reducing tetraphenylarsonium pertechnate, as well as technetium dioxide with hydrogen at the temperature 600°. In this case it turns out in the form of fine-dispersed powder of latently crystalline (non-phanerocrystalline) structure. Its roentgenogram showed a series of diffused lines.

For the purpose to get the greater crystals of technetium metal it needed to heat additionally the samples under vacuum at the temperature 800° during 1 hour. The x-ray diffraction analysis of preparation ascertained[x)] the lattice parameters to be equal to: $a = 2{,}745 \pm 0{,}001$ Å and $C = 4{,}398 \pm 0{,}005$ Å (fig.1), i.e. almost coincident with those reported by Mooney (5). The crystalline structure of metal belongs to hexagonal system with close-packet structure and is analogous to that of magnesium, rhenium, osmium and ruthenium.

Fig. 1

x) The measurements were accomplished by N.A. Shishakov.

349

For analytical determination of technetium the reaction of technetium with α- furyldioxime in hydrochloric acid solution in presence of $SnCl_2$ is studied. The resulting complex compound is crimson-rose coloured. The maximum optical density for 1N (on NCl) solution of technetium corresponds to the wave length $\lambda = 520$ mμ(E=13181) (6).

The complex compound of technetium with methyl-violet is obtained in neutral medium; it is violet coloured, extractible by ethyl acetate and shows the maximum luminous absorption at $\lambda = 582$ mμ (E= 14000).

The compound of technetium with α- benzyldioxide in presence of $SnCl_2$ in 9N solution of sulphuric acid, crimson-rose coloured shows absorption maximum at $\lambda = 495$ mμ(E = 19000).

It is extracted with benzyl and ethyl alcohols.

The complex compound of technetium with o-cyclohexandione-1, 2-dioxime, crimson-rose coloured, forms in 0,5 M solution of hydrochloric acid. The maximum luminous absorption - at $\lambda = 413$ mμ (E = 8780).[x] The sensitivity of reactions varies from 0,07 to 0,1 μg/ml.

We have elaborated for determination of technetium in solution the analytical methods combining selective extraction by acetone with spectrophotometry (the determination error did not exceed 5%) as well as with measurement of absolute counting the beta-particles and application of beta-, gamma-ray spectroscopy. The accuracy of method for this case amounts 10 % (fig.2)[xx]. Furthemore the emission spectral analysis and polarographic analysis were used too.

Fig. 2

x) This part of the work is accomplished by T.S. Taguil.

xx)The physical measurements were accomplished by ~~M.P.~~ Glazunov and P.N. Kodochigov.

349

3. Chemical and electrochemical behaviour of technetium in aqueous solutions

Aqueous solution of chemically and radiochemically pure ammonium pertechnate of concentration 10^{-3} to 10^{-6}M served us in our studies as initial compound for every separate experiment. The study of absorption spectra was carried out in the wave length range 2100–2800 Å. The investigation of behaviour of pertechnate-ion in alkaline and acidic solutions(up to 4N for KOH and NH_4OH, up to 1N for H_2SO_4 and HCl) allowed to ascertain that under such conditions the ion TcO_4^- is sufficiently stable, even when being heated. With increase in alkalinity or in acidity of solutions the essential changes occur both in the shape of absorption spectrum curve and in the value of optical density.

We studied the reduction of ammonium pertechnate ($7{,}1.10^{-6}$M) with hydrazine ($3{,}1.10^{-2}$M). The heating of solution ($t = 90^o$) resulted in appearance on spectrum curve of adsorption maximum at the wave length $\lambda = 231$ mμ. We have found a similar spectrum for technetium-YI compound, formed under coulometric titration of pertechnate solution, where was ascertained the single-electron process of reduction. This part of our work will be described in the following section.

The further protracted heating the sexivalent technetium with hydrazine has led to its reduction into tetravalent state. In ammonia medium, resulted from destruction of excessive hydrazine technetium-IY was oxidized with atmospheric oxygen up to technetium-VII and in absorption spectrum there appeared the maxima distinctive of pertechnate-ion (244, 247 and 287 mμ).

Technetium dioxide reacts with 6N hydrochloric acid under protracted heating ($t = 90^o$, 3 hours) when giving a complex compound – hexachlorotechnate-ion, $TcCl_6^2$ (fig.3).

Fig. 3

349

The experiment conditions indicate the relatively slow dissolution process of technetium dioxide in hydrochloric acid.

The ion $TcCl_6^{2-}$ can also be obtained through reduction of ammonium pertechnate with 4N hyrdochloric acid ($t = 90°$, ~3 hours).

Hexachlorotechnate-ion in neutral ambiance forms hydrated dioxide, which undergoes slowly enough the oxidation by atmospheric oxygen. In alkaline and acid media technetium-IV instantly oxidizes till heptavalent state and the absorption spectrum corresponds then to spectrum of ion TcO_4^-.

The interaction of technetium metal in milligram amounts with concentrated acids – HCl, $HClO_4$ and HNO_3 is studied. The investigation was accomplished by radiometric and spegtrophotometric ways. The insignificance of metal dissolution in hydrochloric acid (5 % from initial amount) was established, what can be explained rather with removing the oxide film, evidently present on the surface of technetium metal. Technetium metal does not react apprecia[illegible] also with perchloric acid, while in nitric acid it is dissolved completely under formation of pertechnetic acid : $Tc + 7\,HNO_3 \longrightarrow HTcO_4 + 7\,NO_2 + 3H_2O$.

The polarographic investigations were devoted to studying the electro-reduction of pertechnate-ions, TcO_4^- and hexachlorotechnate-ions, $TcCl_6^{2-}$ on the dropping mercury electrode.

Polarographic study of the ion TcO_4^- was carried out with diverse 1M background solutions: KCl, KNO_3, NH_4Cl in certain range of solution alkalinity and acidity, as well as in peroxide-alkaline and ammonia media.

The experimental part was carried out in the same sequence, as it was previously described (18). The value of diffusion coefficient is taken from the work (19).

349

The background I M KNO_3

In neutral solution (fig.4) ion TcO_4^- gives the wave of reduction at $\varphi_{1/2} \simeq -0,7$ v, where a great maximum ($\varphi_{1/2} \simeq -1,6$ v), typical for catalytic hydrogen waves, is observed. Calculating the number of electrons by means of Ilkovitch equation at the values of capillary constants: the rate of mercury outlow, m = 1,39 mg/sec and mercury dropping period $\tau = 3,8$ sec has led to n = 3,4. The limiting current of the wave for TcO_4^- is strictly proportional to concentration of technetium for the range $10^{-5} - 10^{-4}$M. The current at the maximum does not depend on the height of mercury column, while at the minimum increases a little with increase of pressure.

Fig. 4

The alkali addition to initially neutral solution produces diminishing the wave height. Thus in 1,1 N solution of KOH the wave of TcO_4^- comes down nearly by one third (n = 1,75 ; $\varphi_{1/2} \sim = -0,8$ v.).

The waves both in neutral and alkaline solution are diffusion controlled ones.

At the careful acidification it has been revealed the appearance of a new diffusion controlled single electron wave ($\varphi_{1/2} \sim = -0,6$ v), whose height with increase of HNO_3 concentrations was still growing till the level of the neutral wave (n = 3) and at the further acidifying the solution it kept continuously increasing , when melting into the background and becoming shifted to positive potentials. No catalytical currents produced by action of oxidizer, nitrate medium, on the product of electro-reduction were found. The waves in highly acid media do not fit for analytical purposes.

The background HCl IM

Process of electro-reduction in neutral solution

349

($\varphi_{1/2} \simeq -0,8v$) is a three-electron and, by its nature, diffusion controlled one (fig.5).

Fig. 5.

In this case a reaction: $TcO_4^- + 3\bar{e} + 2H_2O \longrightarrow TcO_2 + 4OH^-$, which can be used for obtaining technetium dioxide, takes place.

Polarographic study of TcO_4^- in slightly acidic (10^{-4} M HCl) solution (fig.6) has led to appearance of a new single-electron wave (as well as in nitric acid) at $\varphi_{1/2} \simeq -0,6v$ of diffusive character, corresponding to reaction: $TcO_4^- + \bar{e} \longrightarrow TcO_4^{2-}$.

Fig.6

With increase in solution acidity the second wave ($\varphi_{1/2} \simeq -0,6v$) becomes a three-electron one, following the process mechanism: $TcO_4^- + 3\bar{e} + 6Cl^- + 8H^+ \longrightarrow TcCl_6^2 + 4H_2O$. The presence of hexachlorotechnate-ion in solution is confirmed by us spectrophotometrically after a certain amount of $TcCl_6^{2-}$ ions was accumulated by means of electrolysis of 1 ml of solution having composition: 1M KCl + $3,1 \cdot 10^{-5}$ M NH_4TcO_4 + 10^{-3} M HCl at controllable potential, $\varphi_{1/2} \simeq -0,8v$ during 3 hours. The absorption spectrum corresponded to that of ion $TcCl_6^{2-}$, represented by fig.3 and previously reported in literature(10).

The ions of sexivalent technetium were also obtained by coulometry at potential $\varphi_{1/2} \simeq -0,6v$ on the basis of polarogram (fig.6) of initial solution: 1M KCl + $4 \cdot 10^{-4}$M HCl + $0,9 \cdot 10^{-5}$M NH_4TcO_4. The absorption spectrum of technetium_VI is given on the fig.7 Maximum optical density corresponded to wave length $\lambda = 231$ mμ .

Fig. 7.

349

The background IM NH_4Cl

In ammonia solutions (up to 4M NH_4OH). as well as in neutral one, on the background IM NH_4Cl pertechnate-ion is reduced into technetium-IV (n = 3), what can be accounted for by the low alkalinity of NH_4OH solutions applied. In these media the waves of catalytical hydrogen evolution disappear.

The peroxide-alkaline medium

As it is previously shown (18,19), the reduction of pertechnate-ion on the mercury electrode on alkaline solutions in the range of potentials from -0,80 to -0,85V the divarication of wave is observed, when keeping the diffusive nature of current and at the $\varphi_{1/2} \simeq -1{,}6v$ it appears a catalytical hydrogen maximum. The addition of hydrogen peroxide to alkaline solution of ammonium pertechnate (till neutral reaction), as our experiments have shown, the value of limiting current of diffusion controlled wave sharply increases (fig.8, curves 2 and 3).

Fig. 8.

The limiting current i_{lim} of this wave depends linearly upon the concentration of hydrogen peroxide and upon technetium concentration nearly not over the value 3.10^{-3}M NH_4TcO_4, while at higher concentrations the growth of the wave slows down.

Parallel with growth of the height of pertechnate-ion wave in peroxide-alkaline solutions its potential by gradual change of alkaline medium into neutral one becomes more electropositive. All the properties of this wave testify to catalytical nature of its limiting current. Indeed, its height is considerably greater, than that of the wave calculated for a limited diffusion controlled process of pertechnate-ion reduction. Further, its limiting current is

349

independent of mercury column height and greatly grows with increase of temperature. Slowing down the wave growth observed at the higher concentrations of technetium gives also an additional corroboration of its catalytical provenance.

The results of investigation correspond to the following process mechanism. The reduction of pertechnate-ion in alkaline solution (in absence of hydrogen peroxide) at $\varphi_{1/2} \simeq -0{,}85$v follows the equation: $TcO_4^- + 2^-e \longrightarrow TcO_4^{3-}$. When adding hydrogen peroxide, the oxidation of reduced technetium-V into technetium-VII takes place: $TcO_4^{3-} + H_2O_2 \longrightarrow TcO_4^- + 2\ OH^-$. The conditions of electrochemical reduction explored can be advised for analytical determination of technetium and hydrogen peroxide in technetium solutions.

Polarographic study of ion $TcCl_6^{2-}$

Tetravalent technetium in the form of hexachlorotechnate-ion $TcCl_6^{2-}$ has been prepared by the action of 5,5 N hydrochloric acid on ammonium pertechnate on heating the solution ($t = 90^{\circ}$) for 2 hours. The composition of the complex has been confirmed spectrophotometrically.

Polarographic study was applied to 1,5 ml of the solution of the following composition: IM KCl + $1{,}23 \cdot 10^{-4}$M $TcCl_6^{2-}$ + 2,1 N HCl. In this case the wave at $\varphi_{1/2} \simeq -0{,}55$ v with n = 0,89 (~ 1) has been observed. Single-electron reduction has taken place also at the solution acidity of 0,5 and 1,42 N on HCl. The inference of the diffusion nature of the $TcCl_6^{2-}$ wave in hydrochloric solutions is founded on the linear dependence of its limiting current on the height of mercury column (H) in power 1/2. Besides the diffusion wave a great maximum at $\varphi_{1/2} \simeq -1{,}1$ v has been observed on the polarogram.

4. Electrolytic behaviour of pertechnate-ion on the platinum cathode

Some data have been reported on technetium electrolytic

isolation in form of dioxide.

Technetium was previously concentrated from molybdate solutions and from the waste solutions of uranium reprocessing.

In our investigations the solution of purified salt of ammonium pertechnate was electrolyzed in sulphurous (pH 2,3) and ammonium sulphate (pH 5,6) media on platinum cathode. The selection of the latter was determined by the fact that under these conditions one could observe good crystallization of electrolytic deposits of manganeze and rhenium (23,24).

In sulphurous acid solution when the potential was -0,40 v one could already observe considerable rate of technetium isolation, which increased as the potential rises. In the ammonium sulphate solution the technetium electrodeposition proceeded rather intensively beginning with the potential equal to - 0.80 v. In this case the completeness of electrodeposition within an hour was equal to 80%, while in the sulphurous acid medium it corresponded to 45%.

The value of the critical potential of technetium isolation from the sulphurous acid solution, equal to 0,20 v (referred to the normal calomel electrode) has been estimated (fig.9).

Fig. 9

Using the shortened Nernst equation, applied to highly diluted solutions of radioactive salts the standard potential has been calculated by us to be equal to 0.71 v. The value obtained is close to the value of the technetium dioxide potential (TcO_2) reported in literature (10.25).

As a result of the electrolysis of above mentioned solutions a dark film deposit has been at the cathode, which seemed to correspond to the oxide state of technetium. Its roentgenographic analysis does not show the presence of crystalline structure. It appears after heating the

349

samples under vacuum at temperature 800°C,

After the thermal treatment of the specimens roentgenograms have been obtained, when using filtered radiation of copper; on the basis of these roentgenograms comparative roentgenographic characteristics are given (fig.10) containing lines, part of which should be attributed to metallic technetium formed during the electrolysis and partly during the annealing of the oxide by its reduction with hydrogen absorbed in the pores of the precipitate. The rest lines are produced by technetium dioxide, TcO_2.

The calculations made on the basis of roentgenographic measurements give the following parameter values for TcO_2 lattice x)

$$a = 4{,}753 \pm 0{,}005\ \text{Å}$$
$$b = 2{,}840 \pm 0{,}005\ \text{Å}$$

The technetium dioxide crystalline lattice corresponds to tetragonal structure of SnO_2 type and by its dimensions is close to those of MnO_2, MoO_2 and WO_2 lattices.

Fig. 10

Inference and conclusions

The methods of technetium concentration under laboratory conditions from molybdate and waste nitrate solutions have been described, the methods are based on the extraction using acetone, quinoline and tributylphosphate. There are presented the data on the coefficients of technetium purification at its extraction with acetone, quinoline, tributylphosphate and isoamyl alcohol whose values are 10^4, 10^3, 10^2 and 10, respectively.

---

x) The calculation of the parameters of technetium dioxide lattice has been made by N.A. Shishakov.

349

Studied previously colour reactions of technetium with furyldioxime, methyl violet, α- benzyldioxime, o-cyclohexandion-1,2-dioxime are the basis of the analytical methods of determining this element. The sensitivity of reactions is from 0,7 to 0,1 μg/ml.

Analytical means of technetium determination have been developed combining its extraction by acetone with photometry and radiometry.

In neutral and ammonia media, independently of the background composition, the electro-reduction process at $\varphi_{1/2} \simeq -0,7 - -0,8$ v has been shown to be of a diffusion and three-electron nature. At $\varphi_{1/2} = -1,3 \div -1,6$ v there is a catalytic wave whose appearance may be accounted for by the deeper pertechnate-ion reduction. The compound formed appears to catalize the hydrogen evolution by lowering its overvoltage. In favour of the above said is the fact, that on the rhenium metal - the nearest technetium analogue - the hydrogen overvoltage is in fact very low, lower, than on platinum (26). The conditions of the pertechnate-ion electro-reduction may be used for analytical purposes. At $\varphi_{1/2}$ =-0,8v in neutral solution on the background of 1M KCl solution the wave is applicable to coulometry of pertechnate-ion with the aim of accumulating technetium dioxide.

In solutions acidified to 10^{-4}M by nitric and hydrochloric acids there arises a new single-electron wave of pertechnate-ion reduction at $\varphi_{1/2} = -0,6$ v. The experimental conditions have been used to obtain ions of sexivalent technetium in hydrochloric solution. In more acidic (on HCl) solutions the three-electron nature of reduction with the formation of hexachlorotechnate-ion takes place. On the background of 1M KCl solution at $\varphi_{1/2}$ =-0,85 v the pertechnate-ion electro-reduction process corresponds to n = 2.

The presence of catalytic currents owing to the oxidant effect on the pertechnate-ion electro-deposition product in the peroxide-alkaline medium has been ascertained. The linear

349

dependence of the limiting current of the wave on the technetium and hydrogen peroxide concentration has been shown. The wave is applicable for analytical purposes. Polarographic study of hexachlorotechnate-ion in chlorhydric solution indicated the single-electron diffusion nature of process.

Hexachlorotechnate-ions are formed in solution by pertechnate-ion reduction with 4N hydrochloric acid under heating ($t = 90^0$) for three hours and also by coulometry of 1 ml of the initial solution of the following composition: 1M KCl + $3{,}1 \cdot 10^{-5}$M NH_4TcO_4 + 10^{-3}M HCl ($\varphi_{1/2}$ =-0,8 v, duration - 3 hours).

The property of tetravalent technetium to be oxidized by atmospheric oxygen in the alkaline medium gives a chance to obtain pertechnate from technetium dioxide without use of hydrogen peroxide.

The reduction of pertechnate-ion with hydrazine has led to the formation of sexivalent technetium, while at the prolonged heating tetravalent technetium has been formed.

In 1N hydrochloric, sulphuric acid solutions, as well as in 4N solutions of KOH and NH_4OH pertechnate-ion does not undergo essential changes.

The electrolytic technetium isolation carried out in sulphurous acid and ammonium sulphate media has shown technetium to be deposited on the cathode in form of latently-crystalline precipitates. After the thermal treatment of the samples the roentgenograms taken manifested lines both of technetium metal and its dioxide.

Technetium dioxide lattice parameters have been calculated:

$$a = 4{,}753 \pm 0{,}005 \ \text{Å}$$
$$b = 2{,}840 \pm 0{,}005 \ \text{Å}$$

and thus found to be close to those of MnO_2, MoO_2 and WO_2.

349

Approved For Release 2009/08/17 : CIA-RDP88-00904R000100100048-8

Literature

1. Boyd G.E., Larson Q.V., J.Phys.Chem.,64, 988(1960)
2. Gerlit Y.B., Doklady sovietskoi delegatsii na mezhdunarodnoi konferentsii po mirnomu ispolzovaniyu atomnoi energii. Issledovaniya v oblasti geologii, khimii i metallurgii. Geneva (1955), p.202.
3. Rimshaw S.J., Malling G.F., Anal.Chem., 33, 751(1961).
4. Kuzina A.F., Taguil T.S., Zamoshnikova N.N., Spitsyn Vic.I., Doklady Akad. Nauk SSSR, 145, 106(1962); 144, 1066(1962).
5. Mooney R., Phys. Rev., 72, 1269(1947).
6. Kuzina A.F., Zh.Analit. Khimii, 17, 489(1962).
7. Boyd G.E., Cobble J.W., Nelson C.M., Smith W.T., J.Am.Chem. Soc., 74, 556(1952).
8. Fried S., Jaffey A.H., Hall N.F., Glendenin L.E., Phys.Rev., 81741(1951).
9. Rulfs G.L., Meinke W.W., J. Am.Chem. Soc., 74, 235(1952).
10. Boyd G.E., J. Chem. Ed., 36, 3(1959).
11. Grouthamel C.E., Anal. Chem.,29, 1756(1957)
12. Jasim F., Magee R.L., Wilson C.L., Talanta, 2, 93(1959)
13. Miller F.G., Thomason P.F., Anal.Chem., 32. 1429(1960).
14. Schwochau K., Herr W., Z.anorg. allgem. Chem., 318, 198(1962).
15. De Carvalho, R.A.C., Proc.Second U.N.International Conf. on the Peaceful Uses of Atomic Energy, Geneva, Paper No (1958).
16. Parker G.W., Reed J., Ruch J.W., Private communication quoted in Hacney, J.G., J. Chem. Ed., 28, 188(1951).
17. Kuzina A.F., Spitsyn Vict. I.,Zh.Neorgan. Khimii, 5, 1006(1960).
18. Kuzina A.F., Zhdanov S.I., Spitsyn Vict. I., Doklady Akad. Nauk SSSR, 144, 836(1962).
19. Miller H.H. , Kelly M.T., Thomason P.F., Adavances in Polarography, Proceedings of the Second International Congress held at Cambridge, Pergamon Press, Oxford (1960) Vol; II, p. 716.
20. Rogers L.B., J. Am. Chem. Soc., 71, 1507(1949).
21. Cobble J.W., Smith W.T., Boyd G.E., J. Am.Chem.Soc.75,5777(1953)

349

22. Boyd G.E., Larson Q.V., Motta E.E., J.Am.Chem.Soc., 82, 809(1960).
23. Sanzharovskii A.T., Zh. Fiz. Khimii, 35, 20(1961).
24. Suvorova O.A., Dissertatsiya (Institut Fizicheskoi Khimii AN SSSR, Kazakhskii Pedagogicheskii Institut im. Abaya), Moskva, (1962).
25. Cartledge G.H. Smith Wm.T., Jr., J.Phys.Chem., 59, 1111(1955).
26. Pecherskaya A.G., Stender V.V., Zh. Fiz. Khimii, 24, 858(1950).

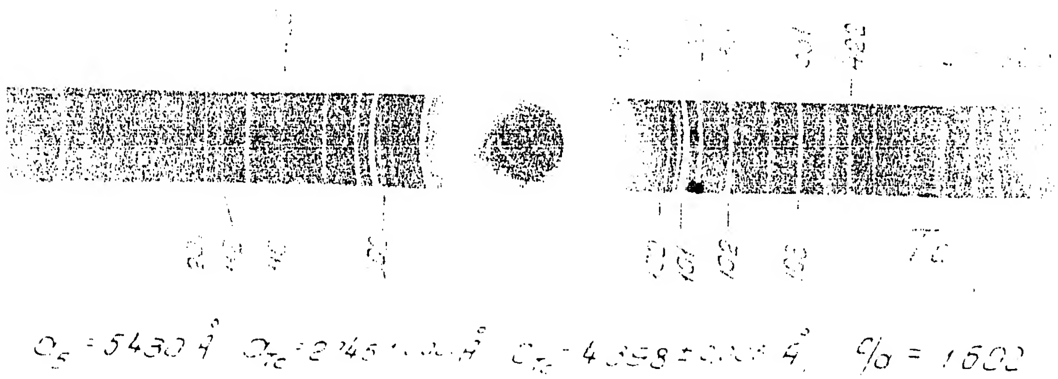


Fig.1. Roentgenogram of a sample of technetium metal.

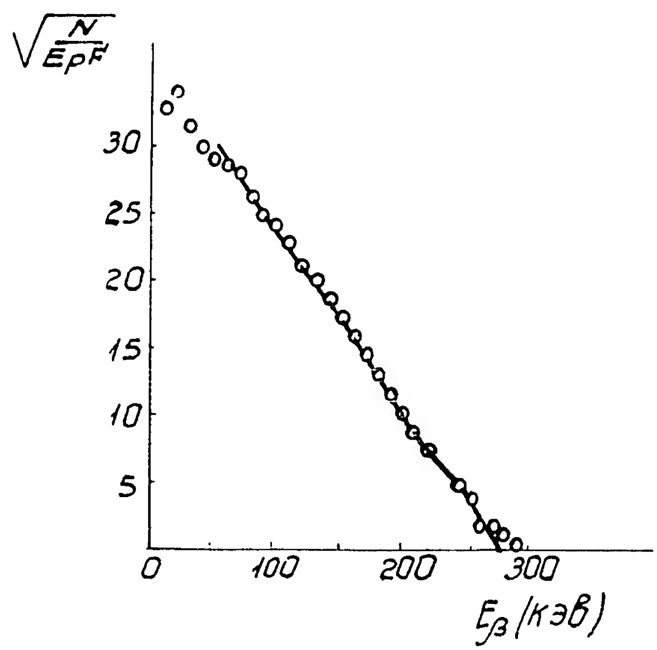


Fig.2. Graph of Fermi for isotope technetium-99 in form of technetium dioxide.

349

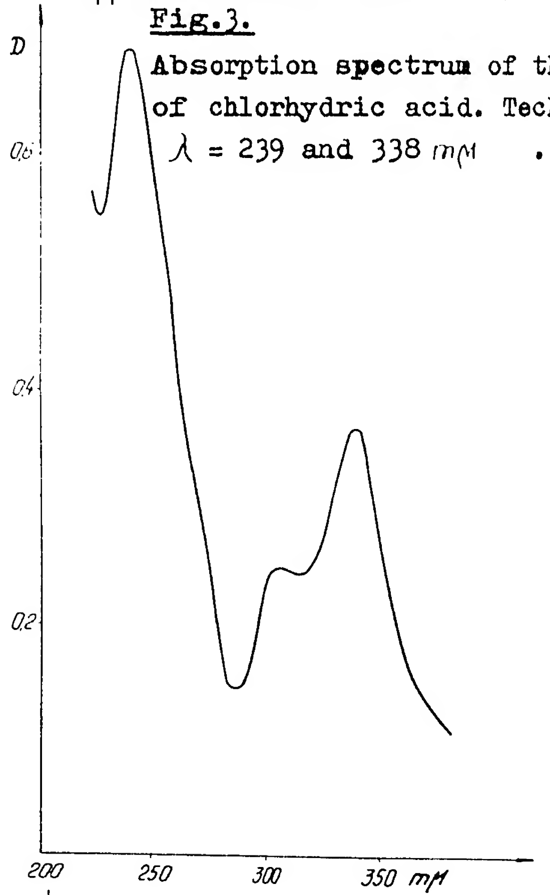


Fig.3.

Absorption spectrum of the ion $TcCl_6^{2-}$ in 6N solution of chlorhydric acid. Technetium concentration 2,4.10^{-5}M. λ = 239 and 338 mμ .

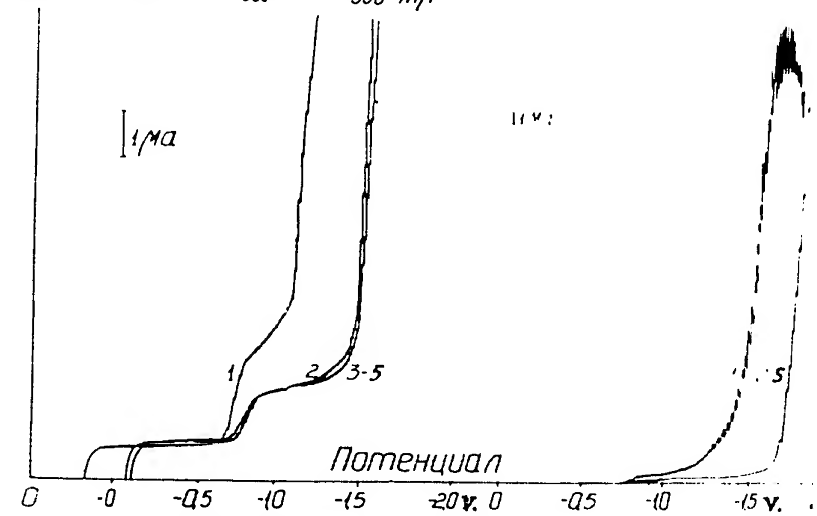


Fig. 4. Polarograms of TcO_4^- in neutral and alkaline solutions on the background of 1M KNO_3.

Composition of solutions: 1. Background (1M KNO_3 + + 0,01 % gelatine) + 1,05 . 10^{-4} M NH_4TcO_4. Alkali concentration: 1. 0; 2. 0,31; 3. 0,62; 4. 0,87; 5. 1,1N KOH.

349

Fig.5. Polarograms of TcO_4^- on the background 1M KCl.

Composition of solutions:

1. Background (1M KCl + + 0,01 % gelatine)
2. Background + $3,1.10^{-5}$M NH_4TcO_4;

acid concentration:

1. 0; 2. 0; 3. 10^{-3}; 4; 10^{-2}; 5. 10^{-1}; 6. 1M HCl.

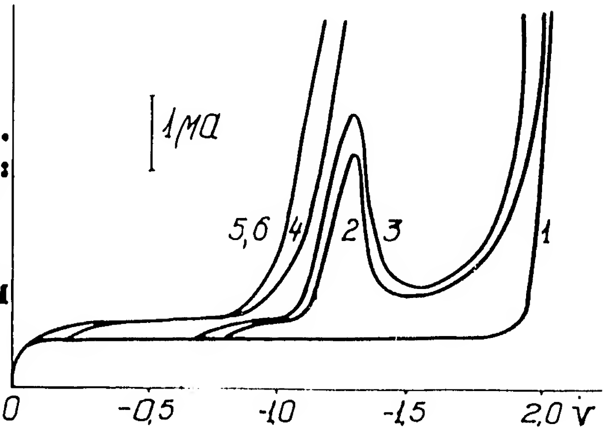


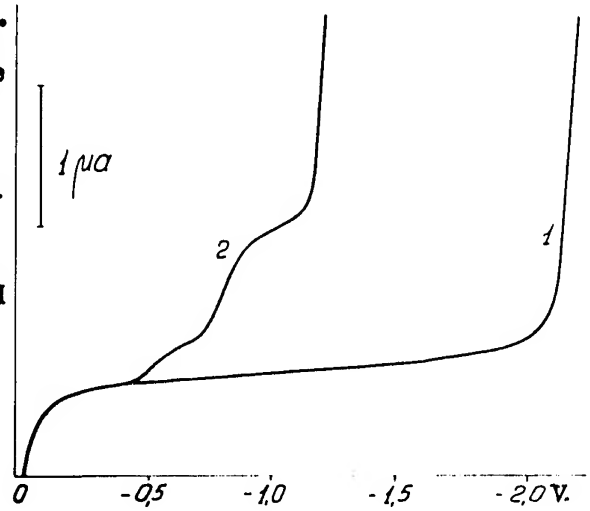
Fig.6. Polarogram of TcO_4^- on the background 1M KCl in slightly acid solution.

Composition of solutions:

1. Background (1M KCl + 0,01% gelatine).
2. Background + $0,9.10^{-4}$M NH_4TcO_4 + 4.10^{-4}M HCl;

m = 0,99 mg/sec ;

τ = 2,4 sec.



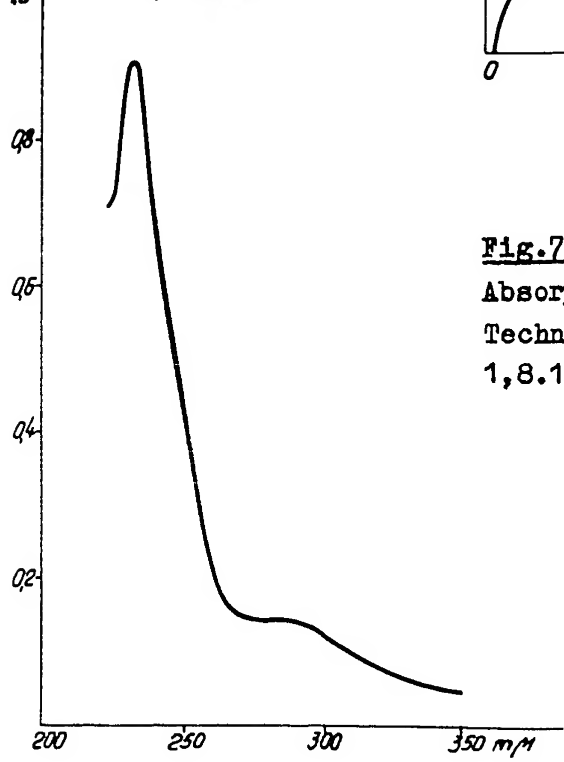


Fig.7.

Absorption spectrum of TcO_4^{2-}.

Technetium concentration $1,8.10^{-6}$M. λ = 231 mμ

Fig.8. Polarograms of TcO_4^- in peroxide-alkaline solution.
Composition of solutions: 1. $7{,}45 \cdot 10^{-5}$M NH_4TcO_4 + + 0,4N KOH
2. $7{,}45 \cdot 10^{-5}$M NH_4TcO_4 + 0,4 N KOH $+ 9{,}5 \cdot 10^{-4}$M H_2O_2
3. -"- -"- -"- $+ 23{,}1 \cdot 10^{-4}$M H_2O_2

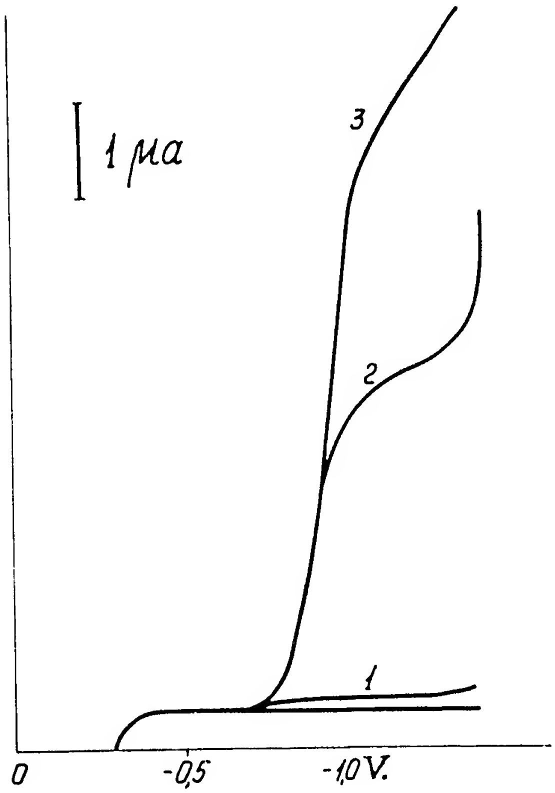


Fig.9.
Dependence of technetium electrodeposition on potential of cathode. Solution of ammonium pertechnate ($2{,}7 \cdot 10^{-5}$M) in sulphurous acid medium. Duration of electrolysis 1. 1;
2. 1,5 hours.

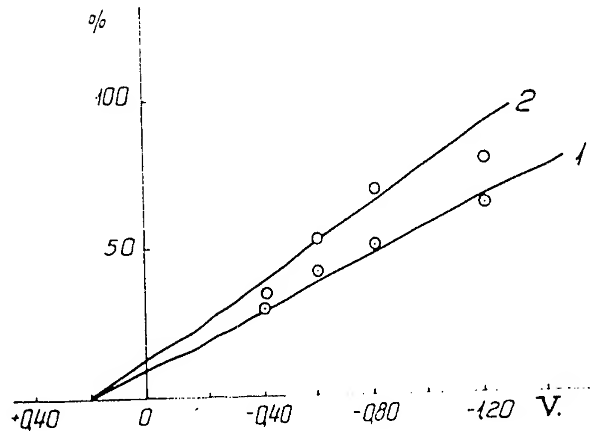
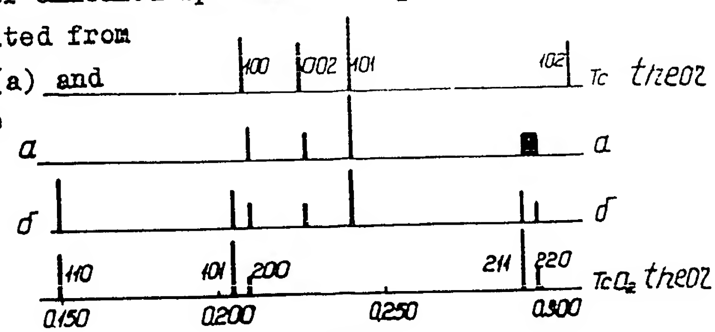


Fig.10. Comparative radiographic characteristics:
calculated - for technetium metal and its oxide,
experimental - for annealed specimens of precipitates electrodeposited from sulphurous acid (a) and ammonium sulphate (b) solutions.



349